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# THE SIGNIFICANCE OF

# PHENOLIC COMPOUNDS

## IN ONTARIO'S WATERS

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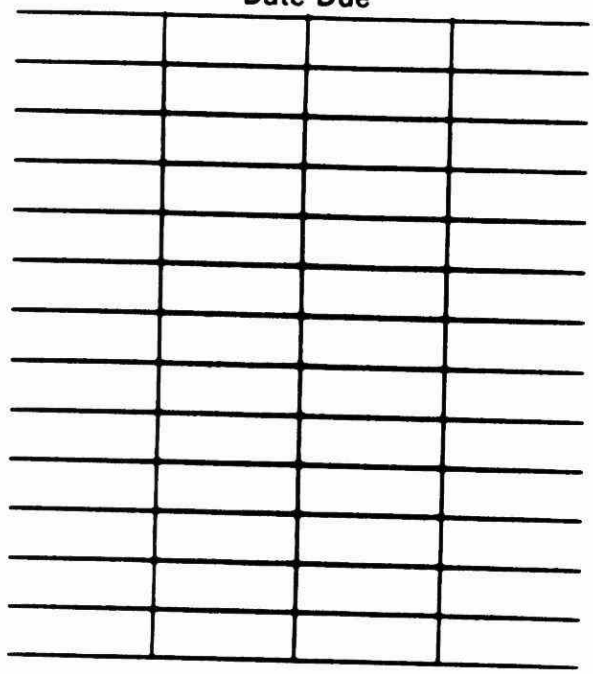

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# THE SIGNIFICANCE OF PHENOLIC COMPOUNDS

# IN ONTARIO'S WATERS

by

CONRAD DE BARROS

Ontario Ministry of the Environment
Water Resources Branch
Aquatic Contaminants Section

August 1, 1984

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# PREFACE

Over the past 2 years the Aquatic Contaminants Unit of the Water Resources Branch has received numerous inquiries from both regional water quality assessors and industrial abatement officers concerning the significance of "phenols" (phenolic compounds) in water. The types of problems MOE staff have with these compounds are reflected in the questions and comments that follow-

- Phenols are typically present in landfill leachate at concentrations greater than the PWQO of 1 ug/L to protect against the tainting of fish-flesh. Considering the location of landfill sites the tainting of fish is not usually of great concern. How should we enforce the PWQO of 1 ug/L in situations like this?

- Without the knowledge of the specific "phenols" present, what concentration of "total phenols" is too much to conscientiously permit discharge to any surface water?

- Is it necessary to request that the individual phenolic compounds be identified? If not, when should the identification of specific phenolic compounds be initiated?

- In our region we have a large zone of non-compliance (exceedance of the 1 ug/L "total phenols" PWQO) with a major fishery downstream which does not appear to be affected by the fish-flesh tainting or toxic properties of phenolic compounds. With this knowledge we simply don't know what to do about this zone of non-compliance.

To help answer many of the concerns about phenols as reflected in these inquiries, an ad hoc working group was assembled.

This group consisted of a regional representative and staff from both the Laboratory Services and Applied Research and Water Resources Branches*. The working group first identified the areas of concern that are common to MOE staff.

The common areas of concern identified were:

1. Phenolic compounds are very poorly understood throughout the Ministry of the Environment.

2. There is confusion as to what kind of analyses is needed for the detection of phenolic compounds in water.

3. The Provincial Water Quality Objectives of 1 ug/L for "total phenols" is exceeded frequently in Ontario's waters.

4. There is a lack of proper guidelines and strategies to help in dealing with such a large group of environmental contaminants which are frequently present in the aquatic environment.

After identifing the common areas of concern, it was decided that these problems be reviewed and the findings reported. It was this Author's responsibility, with the help from the other group members, to carry out this task. The results of the research are presented in this discussion paper entitled "THE SIGNIFICANCE OF PHENOLIC COMPOUNDS IN ONTARIO'S WATERS". It is the Author's hope that this paper will clear up the confusion assosciated with phenolic compounds in water and at the same time provide a basis for further discussion as to a proper strategy in dealing with these aquatic contaminants.

---

* Ad Hoc Working Group Members

| | |
|---|---|
| J. Crowther | J. Ralston |
| C. de Barros | G.A. Rees |
| C. Inniss | D. Veal |
| W.B. Moody III | D. Wells |

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## INTRODUCTION

Phenolic compounds are defined as hydroxy derivatives of benzene and its condensed nuclei. The simplest form of a phenolic compound is monohydroxybenzene (hydroxybenzene) or phenol (see figure 1). Phenolic compounds of both natural and man-made origin are ubiquitous in the environment. These compounds are of environmental concern because of their toxicity to aquatic lifeforms and/or their ability to impart taste and odour to water and fish-flesh.

This review covers the nomenclature of simple hydroxybenzene compounds, analytical problems and solutions for measuring these compounds in aqueous samples, toxicity, environmental fate, organoleptic properties, sources of phenol and its derivatives and a critical review of the existing Provincial Water Quality Objective for "total phenols".

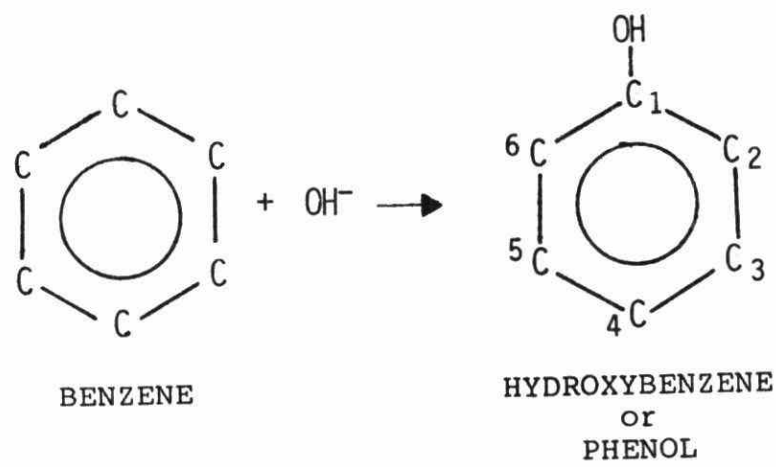



Figure 1

Basic Hydroxybenzene (Phenol) Molecule

## NOMENCLATURE

The substitution of a hydroxyl radical ($OH^-$) onto the benzene ring results in the formation of a chemical compound known as hydroxybenzene or phenol (see Figure 1). Further substitutions of hydroxyl radicals or other substances (i.e. $NH_2^-$, Br, $CH_3$, etc.) gives rise to hydroxybenzene (phenolic) compounds which have different physical, chemical and biological properties than the parent hydroxybenzene (phenol) molecule. In this section the method of naming phenolic compounds that consist of one or more substitutions of a single chemical type (substituent) on the phenol ring is presented.

The number of substitutions of a chemical on the aromatic ring of the hydroxybenzene molecule are indicated by the following prefixes:

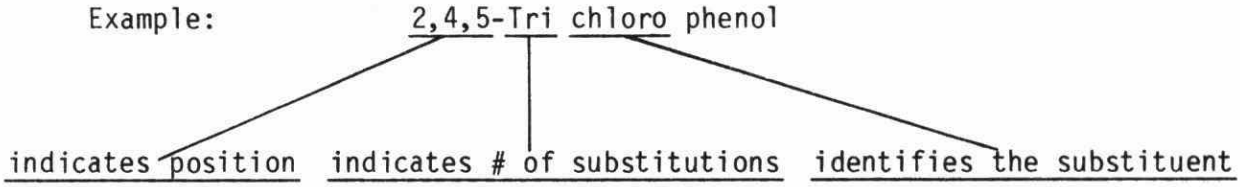
| | | |
|---|---|---|
| one substitution | - | mono |
| two substitutions | - | di |
| three substitutions | - | tri |
| four substitutions | - | tetra |
| five substitutions | - | penta |

The type of chemical compound that is substituted onto the aromatic ring of the hydroxybenzene molecule is indicated by the substituents prefex. For example:

| Substituted Chemical | Substituent Prefix (Type of Phenolic Compounds Formed) |
|---|---|
| Hydroxyl Radical ($OH^-$) | Hydroxyphenols |
| Chlorine (Cl) | Chlorophenols |
| Bromine (Br) | Bromophenols |
| Iodine (I) | Iodophenols |
| Methyl Group ($CH_3$) | Methylphenols |
| Amine Radical ($NH_2^-$) | Aminophenols |
| Nitrate Radical ($NO_3$) | Nitrophenols |
| Methoxy Radical ($CH_3O^-$) | Methoxyphenols |

The carbon positions around the aromatic ring of the phenol molecule are numbered from 1 to 6. The numbering starts at the carbon atom to which the hydroxyl radical ($OH^-$) is attached to because this is the functional group of the parent compound (see Figure 1).

When naming phenolic compounds the position number(s) of the substituents are listed first followed by the prefix indicating the number of substitutions and then the substituent prefix (see table 1). In naming hydroxybenzenes the numbering is kept to the lowest possible numerical combination.




The terms ortho (o), meta (m) and para (p) are used in naming phenolic compounds that have only one substitution on the phenol ring. These terms indicate the position relationship between the hydroxyl radical and the substituted compound. The position relationships are pictorially described in Figure 2a, 2b and 2c.

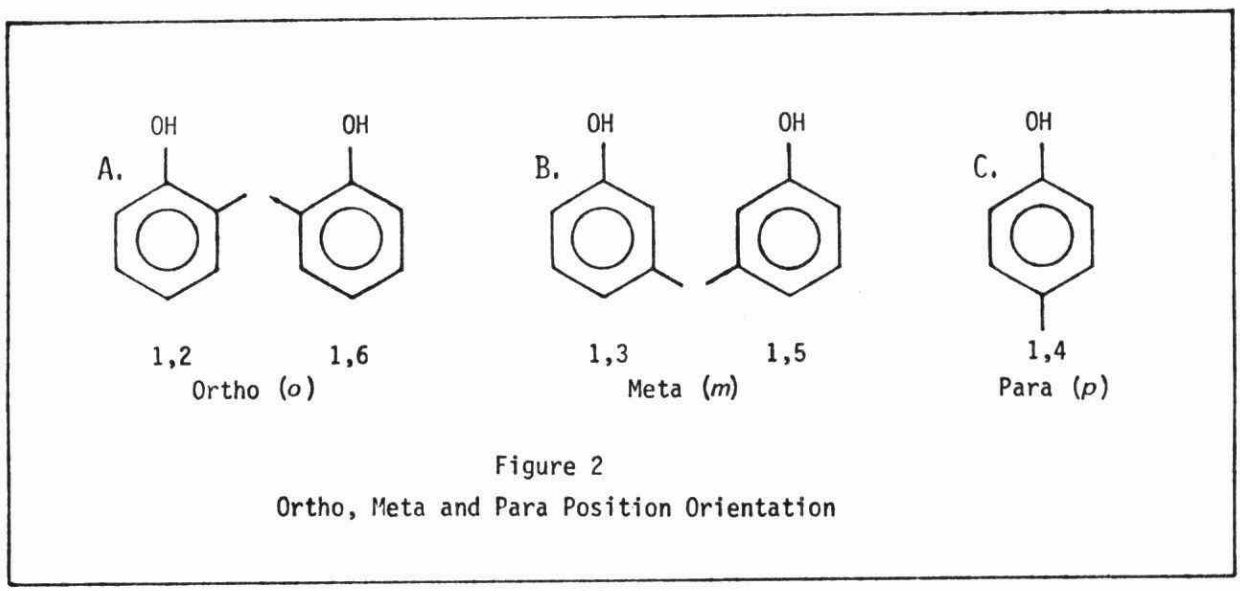
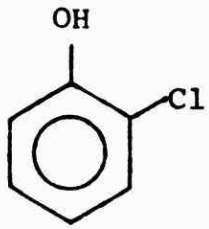
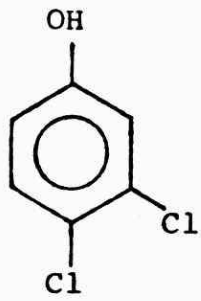
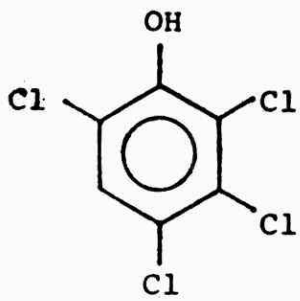
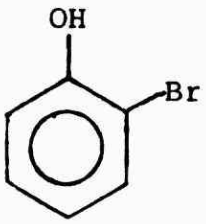
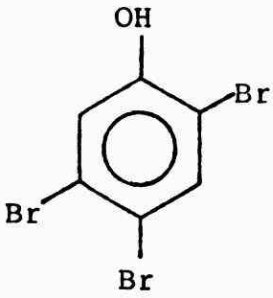
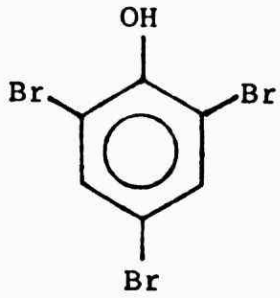
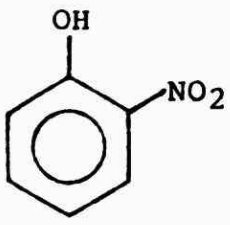
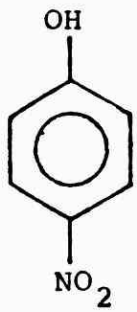
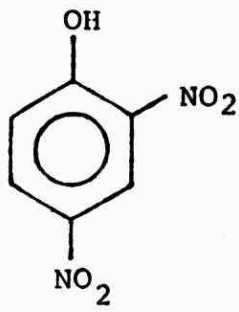



Figure 2
Ortho, Meta and Para Position Orientation

# TABLE 1

## PHENOLIC COMPOUNDS

## (EXAMPLES OF SOME COMPOUNDS THAT ARE FORMED)

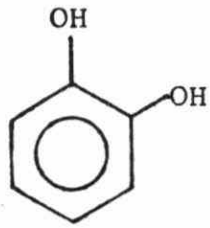
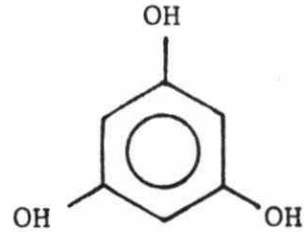
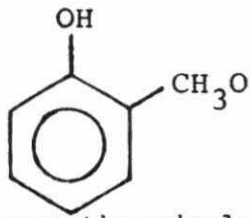
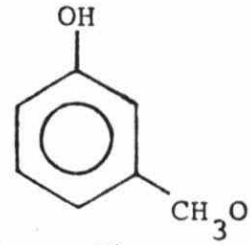
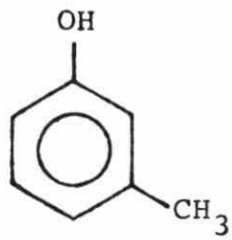
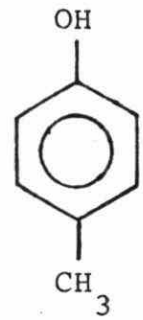
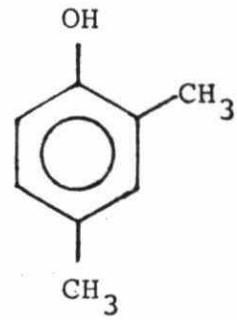
| | | | |
|---|---|---|---|
| CHLORINE ATOM (Cl) |  |  |  |
| | 2-Monochloro-hydroxybenzene<br>2-Chlorophenol<br>*o*-Chlorophenol | 3,4-Dichloro-hydroxybenzene<br>3,4-Dichlorophenol | 2,3,4,6-Tetra-chlorohydroxy-benzene<br>2,3,4,6-Tetra-chlorophenol |
| BROMIDE ION ($Br^-$) |  |  |  |
| | 2-Monobromo-hydroxybenzene<br>2-Bromophenol<br>*o*-Bromophenol | 2,4,5-Tribromo-hydroxybenzene<br>2,4,5-Tribromo-phenol | 2,4,6-Tribromo-hydroxybenzene<br>2,4,6-Tribromo-phenol |
| NITRATE GROUP* ($NO_3$) |  |  |  |
| | 2-Mononitro-hydroxybenzene<br>2-Nitrophenol<br>*o*-Nitrophenol | 4-Mononitro-hydroxybenzene<br>4-Nitrophenol<br>*p*-Nitrophenol | 2,4-Dinitro-hydroxybenzene<br>2,4-Dinitro-phenol |

*Nitrate gives up a O to become $NO_2^-$ when reacting with phenolic compounds.

TABLE 1

PHENOLIC COMPOUNDS

(EXAMPLES OF SOME COMPOUNDS THAT ARE FORMED)

| | |
|---|---|
| HYDROXYL RADICAL ($OH^-$) |  <br>1,2-Dihydroxybenzene<br>*o*-Dihydroxybenzene<br>Catechol<br><br> <br>1,4-Dihydroxybenzene<br>*p*-Dihydroxybenzene<br>Hydroquinone<br><br>  <br>1,3,5-Trihydroxybenzene<br>Phloroglucinol |
| METHOXY RADICAL ($CH_3O^-$) |  <br>2-Monomethoxyhydroxybenzene<br>2,-Methoxyhydroxybenzene<br>*o*-Methoxyphenol<br>Guaiacol<br><br>  <br>3-Monomethoxyhydroxybenzene<br>*m*-Methoxyphenol<br>*m*-Hydroxyanisole |
| METHYL GROUP ($CH_3$) |  <br>3-Methylhydroxybenzene<br>*m*-Methylphenol<br>*m*-Cresol<br><br>  <br>4-Methylhydroxybenzene<br>*p*-Methylphenol<br>*p*-Cresol<br><br>  <br>2,4-Dimethylhydroxybenzene<br>2,4-Dimethylphenol<br>2,4-Xylenol |

## SOURCES

Phenolic compounds in the aquatic environment may occur naturally or as a result of anthropogenic activities. Man-made phenolic compounds enter the aquatic environment in wastewater discharges from municipal sewage treatment plants, pulp and paper mills, petroleum refineries, coal gasification, coke manufacturing, specialty chemical and pesticide manufacturing. Phenolic compounds can also be introduced into the environment through direct application of phenoxy pesticides to agricultural land, as breakdown products of certain plastics, constituents of some landfill leachates, and through the degradation of chlorophenoxy, carbamate and organophosphorus pesticides. The phenolic constituents of wastewater discharges from several industries are listed in Table 2.

In addition to their production and use in industry, a wide variety of phenolic compounds can be formed in nature as minor constituents of essential oils (odoriferous oily products of plant origin). Naturally occurring phenolics can also be formed through the breakdown of plant matter. Lignin is a combination of several polymers that include guaiacyl, syringyl, and p-hydroxyphenylpropane aromatic groups (see Figure 3, NRC Drinking Water and Health Vol. 2). Hydroxybenzene compounds released during the pulping of wood could be termed natural phenolics since they are lignin breakdown products. Chlorination or other chemical modifications in the pulping and bleaching process would place the derivative compounds in the man-made category (Buikema, A.L. Jr. et al). Table 3 lists the concentration ranges of several of these compounds that may be present in pulp and paper mill effluents.

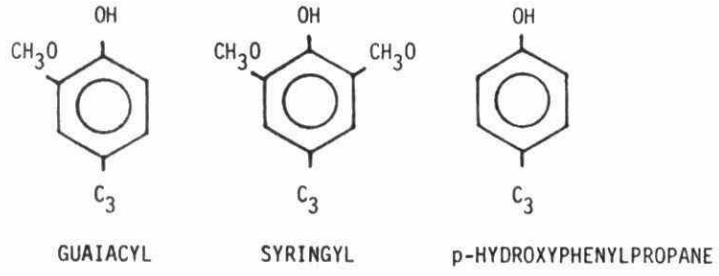



Figure 3
Phenolic Polymer Component of Lignin

Table 2: SUMMARY OF INDUSTRIAL SOURCES

| Type of Industry | Phenolic Compounds Associated With the Industry |
|---|---|
| **Fossil Fuel Industry** | |
| Petroleum Refining | Phenol<br>o-Cresol<br>m-Cresol<br>p-Cresol<br>2,3-Xylenol<br>2,4-Xylenol<br>2,5-Xylenol<br>2,6-Xylenol<br>3,4-Xylenol<br>3,5-Xylenol |
| Coke Manufacturing | o-Cresol<br>m-Cresol<br>p-Cresol<br>Xylenols |
| Coal Gasification | Phenol<br>o-Cresol<br>m-Cresol<br>2,5-Xylenol<br>3,4-Xylenol<br>2,4-Xylenol<br>3,5-Xylenol |
| **Forest Product Industry** | |
| Kraft Pulp Mills | Phenol<br>6-tert-butyl-o-cresol<br>4-Allyl-2, 6-dimethoxyphenol<br>Guaiacol<br>4,5-Dichloroguaiacol<br>2,4,6-Trichlorophenol<br>Vanillin<br>Acetovanillin<br>Homovanillic Acid<br>5-Propyl guaiacol<br>Bis-4-hydroxyphenolmethane<br>2,2-Methylenediphenol<br>4-Methyl-2-tert-butyl phenol<br>p-Hydroxybenzaldehyde<br>Syringaldehyde<br>Acetosyringone<br>Trichloroguaiacols<br>Tetrchloroguaigcols<br>Dichlorocatechols<br>Dichlorophenols |

Table 2: SUMMARY OF INDUSTRIAL SOURCES (continued)

| Type of Industry | Phenolic Compounds Associated With the Industry |
|---|---|
| Forest Product Industry | |
| Wood Preservation | Tetrachlorophenols<br>o-Cresol<br>m-Cresol<br>2,5-Xylenol<br>3,4-Xylenol<br>3,5-Xylenol |
| Dye Manufacturing | Phenol<br>p-Nitrophenol<br>Dinitrophenols<br>p-Aminophenols |

Table 3: CONCENTRATIONS OF PHENOLIC COMPOUNDS IN ONTARIO PULP AND PAPER MILL EFFLUENTS (from a survey of Pulp and Paper Mills June to August 1982, Cherwinsky, C. and Murray, D.)

| Phenolic Compounds | Concentration Range (ppb) |
|---|---|
| Phenol ($C_6H_5OH$) | Nd - 17,000 |
| 2-Chlorophenol | Non-detected |
| 4-Chlorophenol | Non-detected |
| 2,4-Dichlorophenol | Non-detected |
| 2,3,4-Trichlorophenol | Nd - 12.4 |
| 2,4,5-Trichlorophenol | Non-detected |
| 2,4,6-Trichlorophenol | Nd - 15.3 |
| 2,3,4,5-Tetrachlorophenol | Non-detected |
| 2,3,5,6-Tetrachlorophenol | Nd - 4.6 |
| Pentachlorophenol | Nd - 2.2 |
| Guaiacol | Nd - 9,450 |
| Syringaldehyde | Non-detected |
| Vanilline | Nd - 1,656 |
| Homovanillic Acid | Nd - 540 |
| Acetovanillone | Nd - 900 |
| Vanillic Acid | Nd - 720 |
| Acetosyringone | Nd - 19 |
| p-Cresol | Non-detected |
| m-Chloro-p-cresol | Non-detected |
| 2,5-Xylenol | Non-detected |
| 4-AAP Reactive Phenolics (Total "Phenols") | Nd - 3,400 |

## DETECTION OF PHENOLIC COMPOUNDS

### 4-Aminoantipyrine Test

The 4-Aminoantipyrine (4-AAP) Test is a colorimetric test routinely used by the Ontario Ministry of the Environment for the detection of hydroxybenzene compounds (phenolic compounds) in aqueous samples. This test involves the condensation of 4-AAP with hydroxybenzene compounds and subsequent oxidation under alkaline conditions to a coloured product. The colour intensity of the oxidized product is directly proportional to the phenolic concentration provided that a reaction occurs. The use of phenol (hydroxybenzene) as a standard (by the MOE lab) in this colorimetric test means that any colour produced by the reaction of substituted hydroxybenzene compounds is reported as phenol equivalents (MOE Outlines of Analytical Methods).

The number, type and position of substituents on the phenol (hydroxybenzene) ring influence the sensitivity of the 4-Aminoantipyrine Test. As the number of substituents increases on the phenol ring, the reactivity of the phenolic compound is reduced proportionately. Substitutions in the para (4th) position of alkyl, aryl, ester, nitro, benzol, nitroso, amino and aldehyde groups appear to block or inhibit reactions with 4-AAP and are, therefore, not accurately measured in the test (APHA, AWWA and WPCF. Standard Methods). These inherent limitations of the 4-AAP test suggest that only an approximation can be made of the total phenolic concentration in aqueous samples. Since this test depends on the ability of 4-AAP to react with hydroxybenzene compounds it is suggested that the test be renamed the 4-Aminoantipyrine Reactive Test (4-AAP Reactive) to reduce the misinterpretation of the incorrectly named "total phenols test".

Table 3 shows the reactivity of some phenolic compounds with 4-aminoantipyrine (4-AAP) (adapted from unpublished MOE report by W.B. Moody III and K. Hansen).

Table 4: RESPONSE OF PHENOLIC COMPOUNDS TO 4-AMINOANTIPYRINE (4-AAP) AS COMPARED TO PHENOL

| Phenolic Compound | Comparative Response With 4-AAP |
|---|---|
| Phenol | Total response (assume 100%) |
| 2-Chlorophenol | High response |
| 3-Chlorophenol | Medium response |
| 4-Chlorophenol | Medium response |
| 2,4-Dichlorophenol | Medium response |
| 2,5-Dichlorophenol | High response |
| 2,6-Dichlorophenol | Medium response |
| 2,4,6-Trichlorophenol | Low response |
| 2,3,4,5-Tetrachlorophenol | Non-reactive |
| 2,3,5,6-Tetrachlorophenol | Non-reactive |
| Pentachlorophenol | Non-reactive |
| 2-Bromophenol | High response |
| 2,4-Dibromophenol | Medium response |
| 2,6-Dibromophenol | Low response |
| 2,4,6-Tribromophenol | Non-reactive |
| Pentabromophenol | Non-reactive |
| 2-Methoxyphenol | Medium response |
| 3-Methoxyphenol | Medium response |
| 4-Methoxyphenol | Low response |
| 2-Aminophenol | Non-reactive |
| 3-Aminophenol | Non-reactive |
| 2-Nitrophenol | Non-reactive |
| 3-Nitrophenol | Non-reactive |
| 4-Nitrophenol | Non-reactive |
| 4-Cresol | Non-reactive |
| Resorcinol | Medium response |

Total Response to 4-AAP is equal to that for phenol.
Total Response - 100% of the phenolic compound reacts with 4AAP.
High Response - 99%-75% of the phenolic compound reacts with 4AAP.
Medium Response - 74%-50% of the phenolic compound reacts with 4AAP.
Low Response - 49%-25% of the phenolic compound reacts with 4AAP.
Non-Reactive - <25% of the phenolic compound reacts with 4AAP.

Adapted from MOE Laboratory Services and Applied Research Branch Unpublished Report prepared by W.B. Moody and K. Hansen.

Even with its limitations the 4-AAP Reactive test does have some utility as a screening test for the presence of hydroxybenzene compounds in the aquatic environment. To assure analytical accuracy, samples should be collected in specially prepared bottles (Green Labels) containing the proper amount of preservative to inhibit biodegradation and chemical oxidation. Samples should be refrigerated and delivered to the laboratory as quickly as possible. If drinking water is to be chlorinated, samples should be collected from a location just before the chlorination chamber (MOE Outlines of Analytical Methods). If samples are already chlorinated, dechlorination with sodium thiosulphate is needed during sample collection (APHA, AWWA, WPCF. Standard Methods).

Phenolic Speciation

Phenolic Speciation is a test method used to identify individual phenolic compounds in aqueous samples. The methodology for speciating these compounds follows the general steps described in Appendix 1.

This kind of test method is needed when it is necessary to correlate aquatic biological responses and aesthetic qualities to chemical concentrations. Phenolic Speciation should be used to identify specific compounds of concern in cases of:

1) unusually high 4-AAP Reactive test results, and/or
2) industrial effluent impact studies.

The Pesticides Lab. presently performs Phenolic Speciation testing on a routine basis for the higher chlorinated phenolic compounds (trichlorophenols, tetrachlorophenols and pentachlorophenol) and is preparing methods for the routine detection of other speciated phenolics. Implementation of this analytical procedure is expected in the near future.

## TOXICITY

The range of aquatic toxicity for phenolic compounds is very wide. Some phenol compounds are toxic at less than 1 ppm while others exceed several hundred parts per million.

Freshwater fish toxicity information for several phenolic groups is listed in Table 4. Some of these data are listed as ranges because of variance in the reported toxic concentrations. Reasons for the differences in reported toxicities are:

Some toxicity tests were performed with impure compounds. As a result impurities present in the tested phenolic substances may be partially accountable for the toxic effects. This kind of error may have been more prevalent in earlier studies due to the lack of purification and sensitive analytical procedures.

An unsatisfactory experimental procedure may have been employed, especially in earlier tests. Some toxicity testing may have lacked adequate water quality controls, such as dissolved oxygen and pH, to show conclusively that the apparent toxicity was due to the phenol compound under investigation and not other causes. That is, the toxic effects may be attributed to physical or chemical causes other than interaction with phenol.

Researchers have shown that the toxicity of phenolic compounds is affected by both their chemical structure and water quality characteristics (dissolved oxygen, temperature and pH).

### Effects of Chemical Structure on Phenolic Toxicity

The toxicity of phenolic compounds varies with the number, position and type of substitutions on the phenol ring.

Halogenation of the aromatic ring increases the toxicity of phenol with iodo- and bromophenols being more toxic than chlorophenols (Buikema, A.L.). Generally an increasing number of halogen substitutions causes an increase in toxicity (i.e. pentachlorophenol is much more toxic than monochlorophenol). The position of substitution causes a change in toxicity with the para (4th) position being more toxic than the ortho (2nd) and meta (3rd) positions.

Hydroxyl radical ($OH^-$) and methyl group ($CH_3^-$) substitutions also increase the toxicity of the phenol molecule (Buikema, A.L.).

Effects of Water Temperature on Phenolic Toxicity

It has been shown that aquatic organisms tend to be more sensitive to phenolic compounds as water temperature increases (Buikema, A.L). An exception to this generalization is a study by Brown et al (1967) in which the resistance of rainbow trout to phenol and gas-liquor phenolics increased with an increase in temperature of $12^oC$ ($6^oC$ to $18^oC$). The explanation given by Brown was that the rate of excretion of phenol and gas liquor phenolics decreases more rapidly than the rate of accumulation as temperatures are lowered. As a result more of the toxicant is accumulated in the fish at lower temperatures. It is not known if this phenomenon applies to other species or phenolic substances.

Effects of pH on Phenolic Toxicity

Phenolic toxicity does not appear to be affected by intermediate pH levels (i.e. 6 to 8 units). The toxicity of 2,4,5-trichlorophenol and 2,4,6-trichlorophenol were shown to predictably increase with a decrease of the pH value (J. Saarikoski et al, 1981). In another study, phenol was more toxic to crucian carp at pH extremes, however, the effects were partially attributable to the carp's sensitivity to very high and very low pH levels (Buikema, A.L.).

## Effects of Dissolved Oxygen on Phenolic Toxicity

Low dissolved oxygen levels reduce the concentration at which phenolic compounds are toxic to freshwater fish. A study performed by Saroj Gupta et al (revised 1982) showed that the toxicity of phenol, dinitrophenol and pentachlorophenol to a species of freshwater minnow (Notopterus Notopterus) increased with a decrease in dissolved oxygen. The increase in toxicity of these chemicals at low DO concentrations may be explained on the basis that, at low DO levels, fish must pass more water over their gills in order to obtain a sufficient quantity of oxygen, and as a result, the fish absorbs more toxicant via gills than they would at high DO levels. This phenomenon at low dissolved oxygen levels produces lesions in the gills and interferes with the normal gas exchange process (S. Gupta et al revised 1982).

Table 5: TOXICITY OF PHENOLIC COMPOUNDS TO FRESHWATER FISH

| Phenolic Compounds | Species | Concentration | Comments | Reference |
|---|---|---|---|---|
| Phenol | Rainbow Trout | 5.4-9.6 mg/l | 48hr. LC50 | A.L. Buikema Jr. et al. |
| | Bluegill Sunfish | 13.5-23.88 mg/l | 96hr. LC50 | A.L. Buikema Jr. et al. |
| **Chlorophenols** | | | | |
| o-Chlorophenol | Bluegill Sunfish | 8.1-10mg/l | 96hr. LC50 | P.A. Jones Environment Canada. |
| 2,4-Dichlorophenol | Rainbow Trout | 5mg/l at 12.8'C | -death in 3 hrs | P.A. Jones Environment Canada. |
| | Bluegill Sunfish | 5mg/l at 12.8'C | -death in 12 hrs. | P.A. Jones Environment Canada. |
| 2,6-Dichlorophenol | Rainbow Trout | 5mg/l at 12.8'C | -death in 13 hrs. | P.A. Jones Environment Canada. |
| | Bluegill Sunfish | 5mg/l at 12.8'C | -death in 5 hrs. | P.A. Jones Environment Canada. |
| 2,4,5-Trichlorophenol | Bluegill Sunfish | 5mg/l | -death in .5-12 hrs. | P.A. Jones Environment Canada. |
| 2,4,6-Trichlorophenol | Fathead Minnow | .1-1.0mg/l | -death in 96 hrs.TLm | P.A. Jones Environment Canada. |
| Pentachlorophenol | Rainbow Trout | 0.12 mg/l | 96 hr. LC50 | A.L. Buikema Jr. et al. |
| | Fathead Minnow | 0.190-0.230mg/l | 96 hr. LC50 | A.L. Buikema Jr. et al. |
| **Nitrophenols** | | | | |
| o-Nitrophenol | Bluegill Sunfish | 46.3-51.6 mg/l | 48hr.LC50 | A.L. Buikema Jr. et al. |
| m-Nitrophenol | Goldfish | <24.0 mg/l | 8 hr.LC50 | A.L. Buikema Jr. et al. |
| p-Nitrophenol | Goldfish | <10.0 mg/l | 8 hr.LC50 | A.L. Buikema Jr. et al. |
| 2,4-Dinitrophenol | Fathead Minnow | 16.7 mg/l | LC50 | U.S. EPA Nitrophenols. 1980. |
| | Bluegill Sunfish | 0.620 mg/l | LC50 | U.S. EPA Nitrophenols. 1980. |
| 2,4,6-Trinitrophenol | Bluegill Sunfish | 167.0 mg/l | LC50 | U.S. EPA Nitrophenols. 1980. |
| **Methylphenols** | | | | |
| o-Cresol | Fathead Minnow | 12.55-13.42 mg/l | 96hr. LC50 | A.L. Buikema Jr. et al. |
| p-Cresol | Fathead Minnow | 19.0 mg/l | LC50 | A.L. Buikema Jr. et al. |
| 3,4-Xylenol | Fathead Minnow | 14.0 mg/l | 96hr. LC50 | A.L. Buikema Jr. et al. |
| **Hydroxybenzenes** | | | | |
| Catechol | Goldfish | 14 mg/l | -approx. 48 hr. fatal conc. | K. Verschueren. |
| Resorcinol | Goldfish | 57.4 mg/l | -approx. 48hr. fatal conc. | K. Verschueren. |
| Hydroquinone | Goldfish | 0.287 mg/l | -approx. 48hr. fatal conc. | K. Verschueren. |
| Pyrogallol | Goldfish | 18 mg/l | -approx. 48hr. fatal conc. | K. Verschueren. |
| Phloroglucinol | Goldfish | 630 mg/l | -approx. 48hr. fatal conc. | K. Verschueren. |
| **Methoxyphenol** | | | | |
| p-Methoxyphenol | Goldfish | 200 mg/l | -approx. 48hr. fatal conc. | K. Verschueren. |
| **Aminophenols** | | | | |
| p-Aminophenol | Goldfish | 0.2 mg/l | -approx. 48hr. fatal conc. | K. Verschueren. |

## ENVIRONMENTAL FATE AND DISTRIBUTION

The distribution and fate of organic compounds in the aquatic environment depends on a variety of chemical, physical and biological processes (i.e. photolysis, volatilization, sorption, chemical transformation/degradation, and biodegradation). Environmental fate information on the different phenolic compounds is presented in a summary format (Table 6). A brief discussion of the different processes is also presented in this section. Since there is a lack of environmental fate and distribution information on many phenolic compounds, the number of substances in the summary table is limited. Some of the processes have been estimated using physical and chemical properties of specific compounds.

### Photolysis

Photolysis is a chemical process (photochemical reaction) influenced or initiated by light (sunlight), particularly ultraviolet light. Photolytic degradation results in the chemical transformation of a contaminant in the aquatic environment. Two types of photolytic reactions which may occur in the aquatic environment are direct photolysis and indirect photolysis.

Direct photolysis refers to photolytic reactions which occur as a result of a chemical compound absorbing radiation (U.V. light) and undergoing a chemical transformation. Indirect photolytic reactions occur when a second chemical compound absorbs ultraviolet light and initiates a chemical reaction which transforms the chemical compound of interest.

Although water permits the passage of ultraviolet light, the intensity decreases sharply with increasing depths. Photolysis proceeds at very slow rates a few meters below the surface. Factors which affect this process include the ability of chemicals to absorb light energy (photons), the location of contaminants in the aquatic environment (i.e. above or below the point of light extinction), turbidity, and upwelling in lake environments or turbulence in

rivers (vertical mixing). Photolysis tends to be a more significant environmental process for the lower substituted phenolic compounds than the higher substituted phenolics.

Volatilization

Volatilization (evaporation) is defined as a process whereby a chemical is redistributed from the aquatic environment to the atmosphere. A substance's tendency to volatilize from surface waters can be estimated using its vapour pressure and solubility. Generally, chemicals with high vapour pressures and low solubilities will move towards the air, and chemicals with low vapour pressures and high solubilities will remain in the water column. The rate of this process generally increases with higher water temperature, turbulence and factors which increase the solubility (i.e. pH) of environmental contaminants. As molecular size of organic compounds increase, vapour pressures tend to decrease, therefore, volatilization would tend to be of greater importance for the lower substituted phenolic compounds.

Chemical Transformation/Degradation

Chemical transformation/degradation involves the oxidation and hydrolysis of aquatic contaminants. In surface waters oxidation may be affected by water temperature, oxygen concentration and the presence of chemical oxidants (i.e., chlorine, permanganate, alkylperoxyl radicals). Water temperature, pH, metals such as $Cu^{++}$ and particulates influence the rate of hydrolytic reactions. These chemical processes alter the chemical properties (solubility, reactivity) and structure of the reacting chemicals but do not always produce less noxious products. Generally the products of these reactions are more readily biodegraded than the parent compounds, although there are some exceptions (A.M. Stern et al). Chemical transformation/degradation processes occur with most of the phenolic compounds but the environmental rates are uncertain.

## Biodegradation

Biodegradation is the enzyme-catalyzed transformation of chemicals. Bacteria produce enzymes to aid them in the utilization of carbon from chemical pollutants as an energy source. When a pollutant is initially introduced into the aquatic environment there is often a lag period between the exposure of organisms to a chemical and the initiation of biodegradation for some chemicals. This lag or acclimation period may be necessary for the development of appropriate enzyme systems through natural selection or selection processes. An acclimation period may also be observed when there are too few degrading microbes initially available, or more readily metabolizable organic compounds are present. Some organic chemicals are biodegraded only when another organic compound is present to serve as an additional carbon and energy source, this phenomenon is known as co-metabolism (U.S. EPA. Water-Related Environmental Fate of 129 Priority Pollutants. Vol.1, 1979).

For the most part, phenol and phenolic compounds are readily degraded by microbial action in the aquatic environment. Exceptions are the chlorophenols and nitrophenols which are more resistant to biodegradation because of their toxicity to bacteria. Para-substituted nitrophenols and chlorophenols appear to be biodegraded more easily than the ortho and meta forms of these compounds. Generally, phenolics are more resistant to microbial digestion (decomposition) as the molecular weight increases.

## Bioaccumulation

In the summary table (Table 6), bioaccumulation refers to the combined accumulation of contaminants from water to organism (bioconcentration) and organism to organism (biomagnification). Where possible, actual measurements of bioconcentration and/or biomagnification factors (BCF, BMF) are used to indicate the potential of phenolic compounds to accumulate in aquatic organisms. Since there is lack of measured BCFs and BMFs for most of the phenolic compounds the logarithm of the octanol/water partition

coefficient (log P) has been used to estimate the bioaccumulation potential of specific hydroxybenzene compounds (see Table 5).

Table 6: APPROXIMATE BIOACCUMULATION EQUIVALENTS FOR LOG P VALUES

| Bioaccumulation Factor | Log P |
|---|---|
| >4000 X | >6.00 |
| 1000-3999 X | 5.00-5.99 |
| 700-999 X | 4.50-4.99 |
| 300-699 X | 4.00-4.49 |
| <300 X | <4.00 |

Taken from the State of Michigan, Department of Natural Resources, Critical Materials Register, 1980, pp.9

Sorption

Sorption or chemical partitioning between water, sediments and/or suspended particulates occurs in all aquatic environments. The rate of this process is affected by the nature of the chemical pollutant, particle size and organic content of sediments. Finer particle size and higher organic content of aquatic sediments and particulates, increases their ability to sorb chemical pollutants. Chemicals with low vapour pressures and low solubilities tend to be sorbed onto sediments. The octanol/water partition coefficient has been shown to correlate with the sorption potential of chemical pollutants (E.E. Kenag and C.A.I. Goring). In the environmental fate summary (Table 6) the logarithm of the octanol/water partition coefficient has been used, where other pertinent information is lacking, to indicate the potential of specific phenolic compounds to be sorbed by sediments and particulate matter in the aquatic environment.

From the summary table it can be seen that the higher substituted phenolic compounds are more easily adsorbed by sediments and suspended particulates than the lower substituted phenolic compounds.

Table 7: SUMMARY OF AQUATIC FATE OF PHENOLIC COMPOUNDS

| Environmental Processes | Photolysis | Volatilization | Chemical Transformation/ Degration | Biodegradation | Bioaccumulation | Sorption |
|---|---|---|---|---|---|---|
| Phenol | -may be an important degradative process in clear aerated waters | -some phenol may volatilize to the atmosphere | *-oxidation may be important in some aerated surface waters | -significant fate if a sufficient concentration of microorganisms are present | -unimportant based on a log P of 1.46 | -unimportant based a log of 1.46 |
| 2-Nitrophenol | *-slow photolysis may be the main degradative process | -probably unimportant | -oxidation by hydroxyl radical has been demostrated<br>-hydrolysis may be possible if 2-NP becomes sorbed by clay minerals | -resists microbiological degradation by inhibiting aerobic microbial growth of aquatic systems through its action as a oxidative phosphorylation uncoupler | -unimportant based on a log P of 1.76 | -absorption by clay minerals has been demonstrated |
| 4-Nitrophenol | *-slow photolysis may be the main degradation process | -probably unimportant | -oxidation by hydroxyl radical has been demonstrated<br>-hydrolysis may be possible if 4-NP becomes sorbed by clay minerals | -resists microbiological degradation by inhibiting aerobic microbial growth of aquatic systems through its action as a oxidative phosphorylation uncoupler | -unimportant based on a log P of 1.76 | adsorption by clay minerals has been demonstrated |
| 2,4-Dinitrophenol | *-based on information for 4-NP slow photolysis may be the main degradative process | -probably unimportant | -hydrolysis may be possible if 2,4-DNP becomes sorbed onto clay minerals | -may be degraded by isolated cultures but it should also inhibit the aerobic microbial growth of aquatic systems through its action as an oxidative phosphorylation uncoupler | unimportant based on a log P of 1.53 | absoption by clay minerals may take place |
| 2,4-Xylenol | -photoxidation may be important fate in clear aerated waters | -unimportant based on low volatility and high solubility | -oxidation may be relevant in some aerated surface waters in the presence of a metal catalyst | -inconclusive information | -bioaccumulation may be negligible to low based on a log P of 2.50 | -absorption by clay minerals should take place based on a log P of 2.50 but the extent of this is unknown (probably low) |

*-most probable environmental fate(s) based on available information

Table 7: SUMMARY OF AQUATIC FATE OF PHENOLIC COMPOUNDS (Continued)

| Environmental Processes | Photolysis | Volatilization | Chemical Transformation/ Degration | Biodegradation | Bioaccumulation | Sorption |
|---|---|---|---|---|---|---|
| O-Cresol | | -probably negligible based on low vapour pressure and high solubility | -may be oxidized but environmental importance is unknown | *-biodegrades at a moderate rate<br>-soil microflora decomposes o-cresol in one day | | |
| m-Cresol | | -probably negligible based on low vapour pressure and high solubility | -may be oxidised but environmental importance is unknown | *-biodegrates at a moderate rate<br>-soil microflora decomposes m-cresol in one day | | |
| p-Cresol | | -probably negligible based on low vapour pressure and high solubility | -may be oxidised but environmental importance is unknown | *-biodegrates at a moderate moderate rate<br>-soil microflora decomposes p-cresol in one day | | |
| p-Chloro-m-Cresol | *-most probable fate based on the similarity to p-chlorophenol | -probably unimportant | | -degrated by sewage plant treatment the environmental significance is uncertain | -may have a tendency to bioaccumulate based on a log P of 2.95 (probably a low BCF) | -may have a tendency to sorb onto sediments based on a log P of 2.95 |
| 4,6-Dinitro-o-Cresol | *-slow photo oxidation may be the main aquatic fate | -probably unimportant | -hydrolysis may occur if sorption on clay minerals occurs<br>-displacement of the nitro group by a hydroxyl radical may be possible | -occurs in agricultural soils but biodegration may be very slow in surface waters | -may have a tendency to bioaccumulate based on a log P of 2.85 (probably a low BCF) | -may have a tendency to sorb onto sediments based on a log P of 2.53 |
| O-Methoxyphenol | | -probably negligible based on low vapour pressure and high solubility | | *-decomposed by soil microflora in 4 days | -unimportant based on log P values ranging from 1.31 to 2.53 | -unimportant based on log P values ranging from 1.31 to 2.53 |
| m-Methoxyphenol | | | | *-decomposed by soil microflora in 16 days | -unimportant based on log P of 1.58 | -unimportant based on log P of 1.58 |
| p-Methoxyphenol | | | | *-decomposed by soil microflora in 8 days | -unimportant based on log P of 1.34 | -unimportant based on log P of 1.34 |

*-most probable environmental fate(s) based on available information

Table 7: SUMMARY OF AQUATIC FATE OF PHENOLIC COMPOUNDS (Continued)

| Environmental Processes | Photolysis | Volatilization | Chemical Transformation/ Degration | Biodegradation | Bioaccumulation | Sorption |
|---|---|---|---|---|---|---|
| 2-Chlorophenol | *-photolysis has been reported but its significance is uncertaian | probably unimportant at low concentrations based on a moderate V.P. and high solubility | -unimportant | *-does biodegrade; the environmental rate is uncertain (14 days for complete disappearance in a soil suspension) | -unimportant based on a log P of 2.17 | -unimportant based on a log P of 2.17 |
| 3-Chlorophenol | -photolysis has been reported but its significance is uncertain | -propably unimportant based on a low V.P. and high solubility | | *-does biodegrade ( 25 days for complete disappearance from a soil suspension) | -unimportant based on log Ps of 2.47/ 2.50 | -unimportant based on log Ps of 2.47/ 2.50 |
| 4-Chlorophenol | -photolysis has been repoted but its significance is uncertain | -probably unimportant based on low V.P. and high solubility | | *-does biodegrade (9 days for complete disappearance from a soil suspension) | -unimportant based on log Ps of 2.39/ 2.44 | -unimportant based on log Ps of 2.39/ 2.44 |
| 2,4-Dichlorophenol | -insignificant compared with biodegradation | -unimportant based on solubility and vapour pressure | | *-biodegradation has been documented in water and soil suspensions; minimum half-life is 6 days | -may bioaccumulate to low concentrations based on a log P of 2.75/3.08 | -sorption may take place; based on a log Ps of 2.75/ 3.08; this process may be important in the presence of organic material |
| 2,4,5-Trichloropenol | | -probably unimportant | | -biodegradation has been demonstrated in aquatic soils (70% disappearance in 35 days); the rate of this process is uncertain in surface waters | -may bioaccumulate to low concentrations | -log P of 3.72 indicates a potential for sorption by organic particulates -significance of this process is unknown |

*-most probable environmental fate(s) based on available information

Table 7: SUMMARY OF AQUATIC FATE OF PHENOLIC COMPOUNDS (Continued)

| Environmental Processes | Photolysis | Volatilization | Chemical Transformation/ Degration | Biodegradation | Bioaccumulation | Sorption |
|---|---|---|---|---|---|---|
| 2,4,6-Tri-chlorophenol | -photolysis has been reported but its significance is unknown | -probably unimportant | -unimportant | -biodegradation has been demonstrated in aquatic soils (70% disappearance in 9 days); the rate of this process is uncertain in surface waters | probably bio-accumulates to low concentrations | log P of 3.38 indicates a potenial for sorption by organic particulates significance of this process is known |
| 2,3,4,6-Tetra-chlorophenol | probably occurs; significance unknown | | | *-biodegradation in a soil suspension took 72 days for complete disappearance<br>-in a Mississippi lake levels persisted in sediments and soil (half-life: 3.5 months) suggesting slow biodegradation | -may bioaccumulate<br>-calculated BCFs for fish: 330-609 | *-probably important based on a log P of 4.10 |
| 2,3,5,6-Tetra-chlorophenol | probably occurs; significance is unknown | -unimportant | | *-biodegradation has been observed<br>-in a Mississippi lake levels persisted in sediments and soils (half-life: 3.5 months) suggesting slow biodegradation | -may bioaccumulate<br>-measured BCFs in fish livers:40-8,590 | *-probably an important environmental fate process |
| Pentachloro-phenol | *-photolysis has been reported under natural conditions<br>-probably important near the water suface | -probably unimportant | -significance is uncertain<br>-probably unimportant | *-biodegradation has been reported; 72 days for complete disappearance from a soil suspension<br>-PCP may persist for years in organic rich sediments | -may bioaccumlate to high concentrations<br>-measured BCFs range from 10 to 15,00 in fish | *-important process based on a log P of 5.01 |

*-most probable environmental fate(s) based on available information

Table 7: SUMMARY OF AQUATIC FATE OF PHENOLIC COMPOUNDS (Continued)

| Environmental Processes | Photolysis | Volatilization | Chemical Transformation/ Degration | Biodegradation | Bioaccumulation | Sorption |
|---|---|---|---|---|---|---|
| o-Aminophenol | | | | *-decomposed by soil microflora in 4 days | -unimportant based on log P values ranging from 0.37 to 0.55 | -unimportant based on log P values ranging from 0.37 to 0.55 |
| m-Aminophenol | | | | *-decomposed by a soil microflora in less than 64 days | -unimportant based on log P values ranging from 0.04 to 0.22 | -unimportant based on log P values ranging from 0.04 to 0.22 |
| p-Aminophenol | | | | | -unimportant based on a log P value of 0.04 | -unimportant based on a log P value of 0.04 |

*-most probable environmental fate(s) based on available information

Information drawn from U.S. EPA. Water - Related Environmental Fate of 129 Priority Pollutants, Vol. II, and K. Verschueren, Handbook of Environmental Data on Organic Chemicals.

## ORGANOLEPTIC PROPERTIES

Organoleptic properties refer to the ability of a compound to impart taste and odour to water, and to cause tainting of fish flesh as a result of exposure to water contaminanted by the compound. The taste and odour impairment of water and tainting of fish flesh has been related more to organic compounds, particularly chlorinated organics, than inorganic compounds. In most instances, the effects caused by the taste impairment of water and fish are of greater concern for the consumer than the aquatic biota.

The close relationship of the olfactory senses causes difficulty in differentiating taste responses from odour responses. In water, substances must be vapourized in order to impart an odour. Although odorous substances can be tasted, the detection of an odour occurs at a lower level. The lowest concentration at which an odour can be detected is known as the odour threshold concentration. The odour thresholds for some phenolic compounds are presented in Table 7. Certain organic chemicals that are non-volatile and soluble in water can impart their taste characteristics without producing an odour. Chlorination of water containing simple phenol is known to cause an increase in the likelihood of "off flavours" occurring and being detected due to the formation of lower chlorinated phenolic compounds. The taste threshold concentration for phenolic compounds in water are listed in Table 8.

Many organic chemicals including phenolic compounds impart an undesirable flavour in fish-flesh at sublethal concentrations. This flavour impairment occurs as a result of the adsorption of taste impairing pollutants from the water into the fish. Tainting of fish-flesh may also be caused by fish consuming contaminated food (J.S. Alabaster, R. Hoyd). The lowest concentration in water at which a chemical causes a taste in fish-flesh is known as the fish-flesh tainting threshold. The fish-flesh tainting threshold concentration for phenol and other phenolics in water are listed in Table 9.

Table 8: ODOUR THRESHOLD IN WATER

| Phenolic Compound | Estimated Concentration | Reference |
|---|---|---|
| Phenol | >1000 ppb | U.S.EPA. Oct. 1980 |
| | 10,000 ppb | U.S. EPA. Oct. 1980 |
| Chlorophenols | | |
| o-Chlorophenol | 2-3 ppb | Verschueren |
| m-Chlorophenol | 100-200 ppb | " |
| p-Chlorophenol | 33-250 ppb | " |
| 2,4-Dichlorophenol | 0.65-6.5 ppb | " |
| 2,6-Dichlorophenol | 2-3 ppb | " |
| 2,4,5-Trichlorophenol | 11-333 ppb | " |
| 2,3,4,6-Tetrachlorophenol | 915-47,000 ppb | " |
| Pentachlorophenol | 857-12,000 ppb | " |

Table 8: ODOUR THRESHOLD IN WATER (Continued)

| Phenolic Compound | Estimated Concentration | Reference |
|---|---|---|
| **Methylphenols** | | |
| O-Cresol | 71 ppb at 30°C | State of California. WQC. 1963 |
| | 25 ppb at 60°C | " " |
| m-Cresol | 333 ppb at 30°C | " " |
| | 100 ppb at 60°C | " " |
| p-Cresol | 45.5 ppb at 3°C | " " |
| | 200 ppb at 60°C | " " |
| **Methoxyphenols** | | |
| Guaiacol | 21 ppb | Verschueren |

Table 9: TASTE THRESHOLD IN WATER

| Phenolic Compound | Estimated Concentration | Reference |
|---|---|---|
| Phenol | 0.1-20 ppb (Chlorinated Water) | California State. WQC. 198 |
| | 300-60,000 ppb (Unchlorinated Water) | U.S. EPA. OCt 1980 |
| Chlorophenols | | |
| o-Chlorophenol | 0.1-6 ppb (unchlorinated water) | Verschueren |
| m-Chlorophenol | 900-1000 ppb (unchlorinated water) | " |
| p-Chlorophenol | 20-20,400 ppb (unchlorinated water) | " |
| 2,4-Dichloraphenol | 8-20 ppb (unchlorinated water) | " |
| 2,6-Dichlorophenol | 2 ppb (unchlorinated water) | " |

Table 10: FISH-FLESH TAINTING THRESHOLDS

| Phenolic Compound | Species | Estimated Concentrations | References |
|---|---|---|---|
| Phenol | Trout | 25,000 ppb | Verschueren |
| | Carp | 1,000 ppb | |
| Chlorophenols | | | |
| o-Chlorophenol | Rainbow Trout | 60 ppb | Shumway and Palensky |
| | Bluegill Sunfish | 2,000 ppb | Verschueren |
| | Carp | 15 ppb | EFIAC (Schulze) |
| m-Chlorophenol | Carp | 60 ppb | EFIAC (Schulze) |
| | Rainbow Trout | 45 ppb | Shumway and Palensky |
| p-Chlorophenol | Carp | 60 ppb | EFIAC (Schulze) |
| | Fish (unspecified) | 50 ppb | Verschueren |
| 2,3-Dichlorophenol | Rainbow Trout | 84 ppb | Shumway & Palensky |
| 2,4-Dichlorophenol | Rainbow Trout | 1 ppb | " " |
| | Bluegill Sunfish | 14 ppb | " " |
| | Largemouth Bass | 0.4 ppb | " " |
| | Coho Salmon | 10 ppb | Shumway, D.L. |
| 2,5-Dichlorophenol | Rainbow Trout | 23 ppb | " |
| 2,6-Dichlorophenol | Rainbow Trout | 35 ppb | " |
| 2,4,6-Trichlorophenol | Rainbow Trout | 52 ppb | " |
| Pentachlorophenol | -acutely toxic before tainting threshold is reached | | " |

Table 10: FISH-FLESH TAINTING THRESHOLDS (Continued)

| Phenolic Compound | Species | Estimated Concentrations | References |
|---|---|---|---|
| **Methyl Phenols** | | | |
| o-Cresol | Fish (unspecified) | 10,000 ppb (listed as cresols) | Thomas, N.A. |
| m-Cresol | Trout & Carp | 10,000 ppb | Verschueren |
| | Fish (unspecified) | 200 ppb | " |
| p-Cresol | Fish (unspecified) | 10,000 ppb (listed as cresols) | Thomas, N.A. |
| 2,4-Xylenol | Rudd | 1000 ppb (approx.) | Verschueren |
| 3,4-Xylenol | Carp | 5000 (approx.) | " |
| 3,5-Xylenol | Rudd | 1000 ppb (approx.) | " |
| **Hydroxybenzenes** | | | |
| Catechol | Carp | 2500 ppb | Verschueren |
| | Fish (unspecified) | 2000-5000 ppb | " |
| Resorcinol | Carp | 30,000 ppb (approx.) | " |
| Pyrogallol | Fish (unspecified) | 20,000-30,000 ppb | " |
| Phloroglucinol | Fish (unspecified) | 10,000 ppb | " |

Several researchers have shown that there is a lack of correlation between the detection of "phenols" or phenolic compounds in surface waters and any organoleptic effects (Kinney, 1960; Hook 1957; M. German, 1982). Evidence also suggests that taste and odour causing phenolic compounds in water may be formed through the decay of plant material and the subsequent chlorination of these compounds (A.L. Buikema). It should be noted from Tables 7, 8 and 9 that chlorophenols, particularly the monochlorophenols and dichlorophenols, cause taste and odour problems in water, and tainting of fish-flesh at concentrations significantly lower than the other phenolic compounds.

## PROVINCIAL WATER QUALITY OBJECTIVE FOR "PHENOLS"
## A CRITICAL REVIEW

The existing PWQO for "total phenols" (phenolic compounds) states that concentrations should not exceed 1 ug/L to protect against tainting of fish-flesh (Blue Book). This objective is based on the fish-flesh tainting thresholds of o-chlorophenol, p-chlorophenol and 2,4-dichlorophenol which range from 0.1 ug/L to 15 ug/L (o-chlorophenol produced tainting at 0.1 ug/L) (Rationale for the Establishment of Provincial Water Quality Objectives, MOE 1979).

Comparing the 1 ug/L "total phenols" objective with the accumulated information on aquatic toxicity and organoleptic effects of phenolics, it is evident that many of these compounds may exist at concentrations above the 1 ug/L objective without causing any effect. This suggests that the existing PWQO for "total phenols" may be too stringent for the majority of phenolic compounds. On the other hand, some compounds, such as pentachlorophenol, may require objectives that are less than 1 ug/L for aquatic life protection.

A solution to the apparent inadequacy of the present "total phenols" objective is to set objectives for individual phenolic compounds. This approach would be more sensible since it would take the aquatic effects of the specific phenolic compound into consideration, instead of setting an objective based on the effects of three compounds from such a large and varied group of chemicals. To that end, the Water Resources Branch, working in co-operation with the Ministry Standards Steering Committee, has undertaken a program to revise and add to the Provincial Water Quality Objectives. Substance specific criteria for the family of chlorinated phenols have recently been developed and are now undergoing Ministry review. Suggestions as to which groups should be given priority consideration would be welcomed.

# CONCLUSIONS

## Sources:

Phenolic compounds can be of natural and man-made origin. These compounds are present in many industrial discharges and can be formed naturally through the decomposition of plant material.

## Chemical Structure Responses:

The presence of halide, amine, nitrite and other substituents on the phenol molecule dramatically alter the structure of phenolic compounds changing their physical and chemical properties, environmental fate processes, aquatic toxicity and organoleptic effects.

## Detection Methods:

The "total phenols" test currently employed by the MOE (4-AAP) has a limited capability to accurately measure the actual ("true") concentration of phenolic compounds in aqueous samples, many of the speciated forms of phenol are inadequately measured or not detected at all by this test.

Since the "total phenols" test depends on the chemical reaction between 4-aminoantipyrine and the phenolic compounds in an aqueous sample, the name of the test should be changed to the 4-Aminoantipyrine Reactive test.

To effectively evaluate the potential environmental effects of phenolic compounds, it is necessary to identify the speciated phenolic forms in an environmental sample.

Presently, MOE laboratory capabilities for routine phenolic speciation is limited and requires special arrangements with the lab. This reflects a need for the development of methodologies for routine speciation testing for phenolic compounds.

Provincial Water Quality Objectives:

Based on the accumulated toxicity and organoleptic information for a variety of speciated phenolic compounds and with specific reference to the recommended objectives recently developed for chlorinated phenols (see Appendix 2), the existing PWQO value of 1 ug/L for "phenols" is of limited value.

To derive appropriate PWQO's for this class of chemicals, objectives should be set for individual phenolic compounds (this approach to setting objectives depends greatly on the support of phenolic speciation testing by MOE labs).

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# APPENDIX 1

# REVIEW OF GENERAL APPROACHES TO PHENOL SPECIATION

Gerald A.V. Rees - May, 1984

Many speciation methods for phenols have been used in environmental work. These methods normally comprise the following general steps.

1. Extraction/Recovery of the phenols from water.
2. Conversion of phenols to easily analysable form (usually only necessary for GC analysis).
3. Removal of interfering substances.
4. Separation of complex phenol/phenol derivative mixtures into individual compounds by Gas Chromatography High Pressure or liquid Chromatography.
5. Detection and identification of individual phenols either by retention index, or by specific detected/structure related response together with retentive index cross correlation.
6. Quantitation of phenol by using pre-constructed calibration curve.

## Extraction

Phenols can be recovered from an aqueous sample by solvent extraction at low pH or by adsorption onto a suitable resin (either macroreticular polymer or ion exchange type), followed by solvent desorption. The solvent extracts from any of the above extraction methods are then normally concentrated by evaporation.

## Derivatization

Phenolic compounds can be analysed directly, either by HPLC, or by capillary gas chromatography. However, to improve detection specificity and sensitivity and chromatographic properties for gas chromatography (GC), derivatization is frequently used to convert the acidic phenol group to a less polar moiety. Methylation,

silylation, acetylation, pentaflurobanzylation, trifluroacetylation etc., have all been used to produce easily chromatographed phenolic derivatives. Some of the procedures are carried out on the phenolic concentrate after solvent extraction. Some reactions are carried out in the aqueous phase before extraction.

Clean Up

Most preliminary cleanup methods use acid/base/solvent partition steps. This procedure can isolate the acidic/phenolic components from other contaminants. Specific well controlled pH conditions can permit further separation of the acidic from the phenolic compounds.

Separation

This is normally accomplished by gas chromatography or high pressure liquid chromatography (HPLC). The former, especially with inert high resolution fused silica capillary column, has excellent capability to resolve highly complex phenol mixtures. The latter has been fairly widely used for phenol analysis, but cannot yet achieve the separation for efficiency of GC on a routine basis. Costs and maintenance were also higher for HPLC.

Detection/Identification

Capillary GC uses a wide range of detectors for phenol analysis. These detectors vary greatly in their sensitivity, accuracy and degree of specificity. Flame Ionization Detection (FID) is generally applicable and sensitive, but gives no structural specificity, and requires significant clean-up. Electron Capture and Hall detectors have higher sensitivity than FID, and are specific for halogenated phenols and nitro phenols. Phenols with no electronegative substitutes give very low or no responses using this detector. Mass spectrometry would probably be the best all round structurally specific GC detector for phenols. It has high sensitivity, can identify each phenol by structure and can be accurately calibrated. However its cost, and lack of routine automation make it an impractical option for routine phenol monitoring and speciation.

HPLC detector can have considerable specificity for phenols. Ultraviolet (UV) detection at 254 nm will pick up most phenols with little or no selectivity. Fluorescence detection can be very specific but requires a complex programmable detection system for broad spectrum phenol speciation. HPLC with UV detection has been used by the ministry for speciation of non-chlorinated phenolics from pulp and paper processes.

Quantitation

This is normally carried out on all the above detectors (GC or HPLC) by construction of a calibration curve using the appropriate standard material. Unless the clean-up/instrumental-separation method can resolve interferences from most common phenols, this calibration can only be carried out after a preliminary qualitative analysis. A high resolution clean-up/capillary GC separation however, frequently provides enough separation for the use of a complex 30-40 component standard, and corresponding calibration for all compounds in the standard prior to analysis. Direct readout of concentration from the first sample run is often possible.

Selection of Candidate Method for Broad Spectrum Phenol Speciation

Non halogenated/nitrated phenols respond poorly or not at all to the Electron Capture (EC) detector. Identification of these compounds thus relies exclusively on retention index as measured by the FID detector only. Halogenated phenols will produce a response on both FID & EC detectors. Identification can thus use the retention index, and also the ratio of responses on both detectors; another feature which is characteristic of the molecular formula and degree of chlorination of the phenolic compound under study.

# APPENDIX 2

# PROVINCIAL WATER QUALITY OBJECTIVES: CRITERIA DEVELOPMENT DOCUMENT FOR CHLORINATED PHENOLS

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## SUMMARY


### Background

In this report, the chlorophenols (CP's) are divided into five major groups of isomers - monochlorophenols (MCP's), dichlorophenols (DCP's), trichlorophenols (TCP's), tetrachlorophenols (TTCP's) and pentachlorophenol (PCP). CP's are commercially used as biocides or as intermediates in biocide production. These compounds are introduced to surface water environments primarily in discharges from forest products industries, sewage treatment plants and agricultural systems.

Because of their toxic properties and potentially widespread occurrence in the environment, the need to establish criteria for the protection of aquatic ecosystems was recognized. This report reviews the behaviour and toxicity of CP's in freshwater environments, and recommends criteria for the protection of aquatic life in freshwater ecosystems from CP contamination.

### Environmental Fate

Table 1 provides an overview of the relative importance of various environmental processes affecting the removal and breakdown of CP's in surface waters. These processes may be divided into two groups - degradation processes that alter the chemical structure of CP's and transport processes that remove CP's from the water column.

Among degradation processes, biodegradation by microorganisms appears to be the most important breakdown process for all CP's. Rates of biodegradation depend on water quality conditions (temperature, flow, dissolved oxygen level) and generally increase with increasing chlorination of the phenol ring (Alexander and Aleem 1961). Photolysis may be a significant degradation process for PCP in shallow, neutral to alkaline waters. Photolysis of other CP isomers has been reported, but its importance under environmental conditions is unknown. Chemical degradation without microbial or photolytic processes is thought to be insignificant in the environment.

The two abiotic transport processes considered are sorption and volatilization. All CP's tend to adsorb onto particulates in the water column, especially where the particulate organic level is high. Enrichment of nearly all isomers in sediments has been observed in

TABLE I: SUMMARY OF AQUATIC FATE OF CHLOROPHENOLS

| | Monochlorophenols | Dichlorophenols | Trichlorophenols | Tetrachlorophenols | Pentachlorophenol |
|---|---|---|---|---|---|
| **Degradation Processes** | | | | | |
| Photolysis | demonstrated in laboratory; environmental significance unknown. | probably insignificant in natural waters | process has been reported; environmental relevance unknown. | process apparently unreported for TTCP probably occurs to some extent; environmental relevance unknown. | of some importance in neutral to alkaline conditions, particularly in shallow, clear waters. |
| Biodegradation | reported in laboratory for all isomers; rate in environment uncertain | a well-substantiated process; rate depends on water quality and adaptation of bacteria. | reported in water, soil and bacterial cultures; probably occurs more readily in stagnant waters than in dilute or flowing systems. | reported in soil and bacterial cultures; TTCP persisted in sediment and water of a contaminated Mississippi lake, suggesting slow biodegradation in aquatic systems. | reported in aquatic conditions and in bacterial cultures; favoured by high temperatures and aerobic conditions. |
| Chemical Degradation | hydrolysis and oxidation considered unimportant. | oxidation and hydrolysis reactions are probably insignificant. | oxidation and hydrolysis reactions are probably insignificant. | oxidation and hydrolysis reactions are probably insignificant. | oxidation and hydrolysis reactions are probably insignificant. |
| **Transport Processes** | | | | | |
| Sorption | show some tendency to associate with particulates, based on log P values (2.19 to 250) and on observed sediment contamination in the Rhine River. | may be of some importance in organic particulates based on a log P of 2.75-3.08; sediment accumulation of various DCP's observed in Rhine River sediments. | probably important based on log P of 3.72 for 2, 4,5- and 3.38 for 2,4,6-TCP; sediment enrichment observed in Rhine River and Finnish lake sediments,. | probably important based on log P of 4.10 for 2,3,4,6-TTCP; sediment enrichment reported in a Mississippi lake, the Rhine River and a Finnish lake. | important based on log P of 5.01 (undissociated PCP); sorption more favoured under acidic conditions; sediment enrichment observed in contaminated environments. |
| Volatilization | probably of low environmental significance. | not considered important in natural surface waters. | not considered important in natural surface waters. | not considered important in natural surface waters. | probably of minor importance in shallow waters at pH 5; of negligible importance under neutral or alkaline conditions. |
| Bioaccumulation | theoretical BCF 7 to 70X based on log P, measured BCF in bluegill, 214 times. | reported in marine biota and crop plants; calculated BCF = 39 to 67 based on log P of 2.92 | 2,4,5-TCP: BCF = 170-1,900 (fish); 2,4,6-TCP: BCF = 51-4420 (plants), 115-12,180(fish), 3,000 (invertebrates). | BCF calculated from log P = 330-609 (fish); measured BCF, sunfish, bass, catfish - 20-221 (muscle), 40-8,590(liver), leeches - 10,000, Cladophora - 1,250. | measured BCF's range from 10 to 15,000 in fish, highest values in liver; whole body and muscle BCF ≤1,000 in most fish; up to 15,000 in Bay of Quinte fish, lower in algae and invertebrates; usually ≤ 500 for fish muscle; calculated BCF's based on log P of 5.01 are higher than measured values; BCF in algae = 1,250. |
| **Probable Environmental Half-life** | <1 - 26 days | ≥6 days | >9 to >35 days | >3.5 months, possibly years in organic-rich sediments | <3.5 months (aerobic conditions) to years in organic-rich sediments. |

the environment (e.g., Wegman and Broek 1983). The affinity of CP's for particulates increases somewhat with increasing chlorination. However, increasing pKa values with increasing chlorination indicate that the higher chlorinated compounds tend to be ionized at neutral pH, thereby reducing their octanol solubility (Hansch and Leo 1979). Consequently, their affinity for organic matter in sedimentary materials is also reduced. Volatilization of all CP's from the water column is probably of low importance for removal from the water column.

All CP's bioconcentrate in aquatic biota. Bioconcentration factors (BCF's) are highly variable, depending on the species studied and on experimental procedure. Calculated BCF values based on octanol-water partition coefficients suggest increasing BCF's with increasing phenol chlorination. BCF values are generally lower in MCP's and DCP's (up to about 200 X) than in the higher CP's, with the highest observed values exceeding 10,000 X (2,4,6-TCP). Observed BCF's usually do not exceed 1000 X for all CP's. Liver tissue is usually characterized by a higher BCF than those for muscle or whole fish. Rates of CP uptake from water are relatively rapid in fish. When returned to clean water, the depuration of CP's by fish is relatively rapid for MCP and DCP ($T_{1/2} < 2$ days), but may be slower for TCP, TTCP and PCP ($T_{1/2} < 10$ days).

Overall half-lives for CP's in aquatic environments, based primarily on biodegradation, are relatively short. Half-lives appear to range from days for MCP and DCP to weeks for TCP and months for TTCP and PCP (Table 1).

**Effects on Aquatic Organisms**

Table 2 summarizes the lowest criteria reported for acute and chronic toxicity in aquatic animals, toxicity to plants and flesh-tainting thresholds for the five CP isomer groups. The most obvious trend illustrated in this table is the increasing acute toxicity with increasing chlorination. Thus, the lowest $LC_{50}$ values for MCP's are 2100-3830 ug/L, and the lowest value for PCP is 55 ug/L. Fish flesh tainting thresholds also tend to decrease with increasing chlorination. Tainting thresholds for MCP and DCP are much lower than levels causing acute and chronic effects. Shumway and Palensky (1973) could not reach a tainting threshold for PCP in test fish without causing acute lethality.

Another important trend noted in specific studies, but not apparent in Table 2, is a decrease in CP toxicity with increasing pH (e.g., Holcombe et al. 1980). CP's tend to

TABLE 2: SUMMARY OF LOWEST TOXICITY VALUES[1] (ACUTE, CHRONIC AND PLANT TOXICITY) AND FLAVOUR IMPAIRMENT THRESHOLDS FOR CHLOROPHENOLS

| Chlorophenol | Acute | | Chronic | | Plant | | Tainting |
|---|---|---|---|---|---|---|---|
| | Value | Species | Value | Species | Value | Species | Threshold |
| Monochlorophenols | | | | | | | |
| 2-CP | 2100 | rainbow trout | 3900 | fathead minnow | 500 mg/L | green alga | 15 |
| 3-CP | 2900 | rainbow trout | - | - | - | - | 15 |
| 4-CP | 3830 | bluegill | - | - | 4790 | duckweed | 15 |
| Dichlorophenols | | | | | | | |
| 2,4-DCP | 1480 | goldfish | 70 | rainbow trout | 50 mg/L | green alga | 0.4 |
| Trichlorophenols | | | | | | | |
| 2,3,5-TCP | 450 | bluegill | - | - | 10 mg/L | green alga | - |
| 2,3,6-TCP | 320 | bluegill | 720 | fathead minnow | 5920 | duckweed | 52 |
| Tetrachlorophenols | | | | | | | |
| 2,3,4,6-TTCP | 140 | bluegill | - | - | 603 | duckweed | - |
| 2,3,5,6-TTCP | 170 | bluegill | - | - | 2660 | green alga | - |
| Pentachlorophenol | 55 | coho salmon | 1.61 | sockeye salmon | 7.5 | green alga | - |

[1]All values expressed in ug/L unless otherwise indicated.

dissociate to chlorophenate ions in water and the degree of dissociation depends on both the pH of the water and on the dissociation constant of the specific CP isomer. The degree of dissociation increases with pH. The lower CP's do not dissociate as readily as the higher CP's at normal environmental pH. Because the dissociated forms of CP's are considerably less toxic than the undissociated forms, increasing pH tends to decrease CP toxicity.

Although few studies have examined the effect of water hardness on CP toxicity, the available data indicate that toxicity is not appreciably diminished by increasing hardness (e.g., Birge et al. 1979).

**Recommended Criteria**

The surface water quality criteria recommended for the protection of aquatic biota are summarized in Table 3. These values are based on acute and chronic toxicity data and on threshold concentrations for the tainting of fish flesh. All values are derived to protect the most sensitive Ontario species from both toxicity (acute and chronic) and flavour impairment.

The most sensitive response of aquatic biota to MCP and DCP is flavour impairment. Recommended criteria are, therefore, less than the lowest tainting thresholds for these lower CP's. The conventional approach of using acute toxicity data and standard application factors to derive criteria would not protect aquatic biota from flavour impairment.

The recommended criterion for TCP is based on the lowest acute $LC_{50}$ value multiplied by an application factor of 0.05 for non-persistent contaminants. Non-persistent toxic contaminants are those having half-lives in surface water environments of less than eight weeks, as stipulated by the International Joint Commission in the Great Lakes Water Quality Agreement of 1978.

Recommended criteria for TTCP and PCP are based on the lowest acute $LC_{50}$ values multiplied by an application factor of 0.01 for persistent contaminants. Persistent toxic contaminants, as defined by the International Joint Commission, have half-lives of greater than eight weeks in surface water environments.

TABLE 3: RECOMMENDED SURFACE WATER CRITERIA FOR CHLOROPHENOLS

| Chlorophenol | Recommended Criterion[1] (ug/L) | Basis |
|---|---|---|
| Monochlorophenols | 7 | flavour impairment |
| Dichlorophenols | 0.2 | flavour impairment |
| Trichlorophenols | 18 | acute toxicity, non-persistent |
| Tetrachlorophenols | 1 | acute toxicity, persistent |
| Pentachlorophenol | 0.5 | acute toxicity, persistent |

[1]Criteria are applicable to all isomers within each chlorinated class.

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